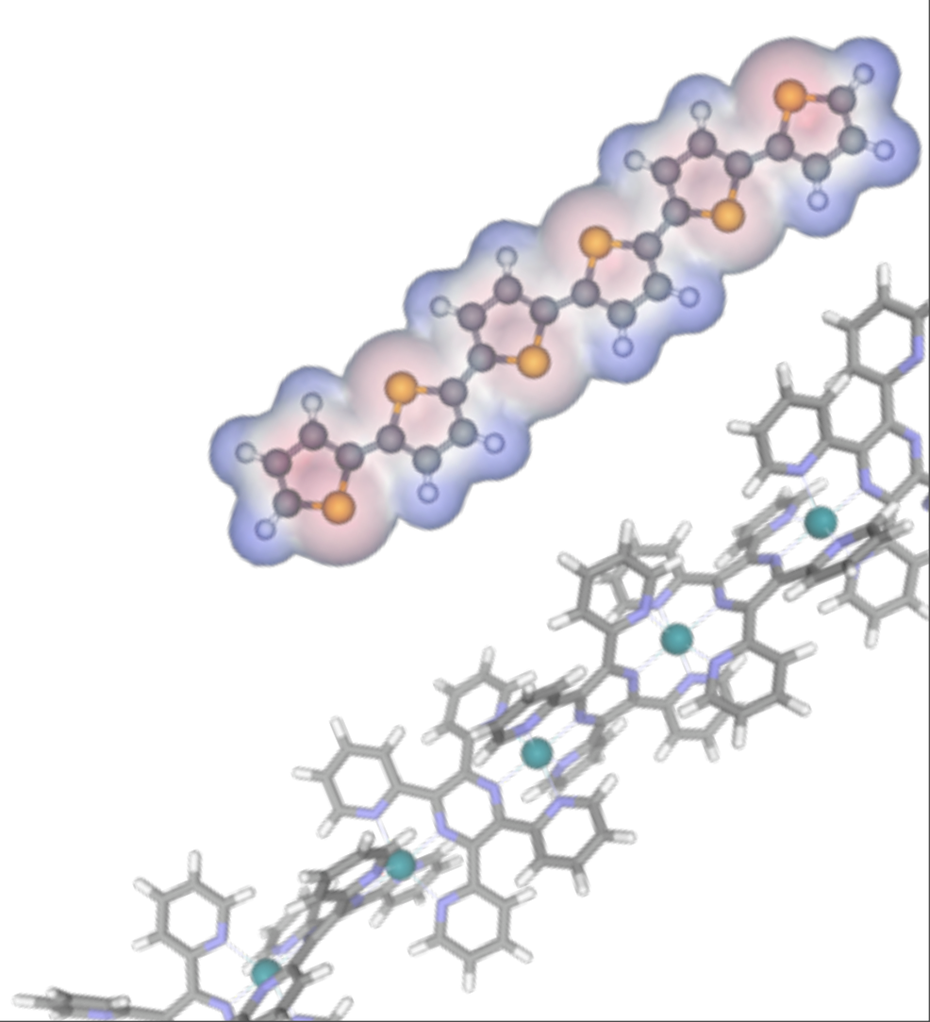
Charge Transport 101: A Few Major Mechanisms



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Outline

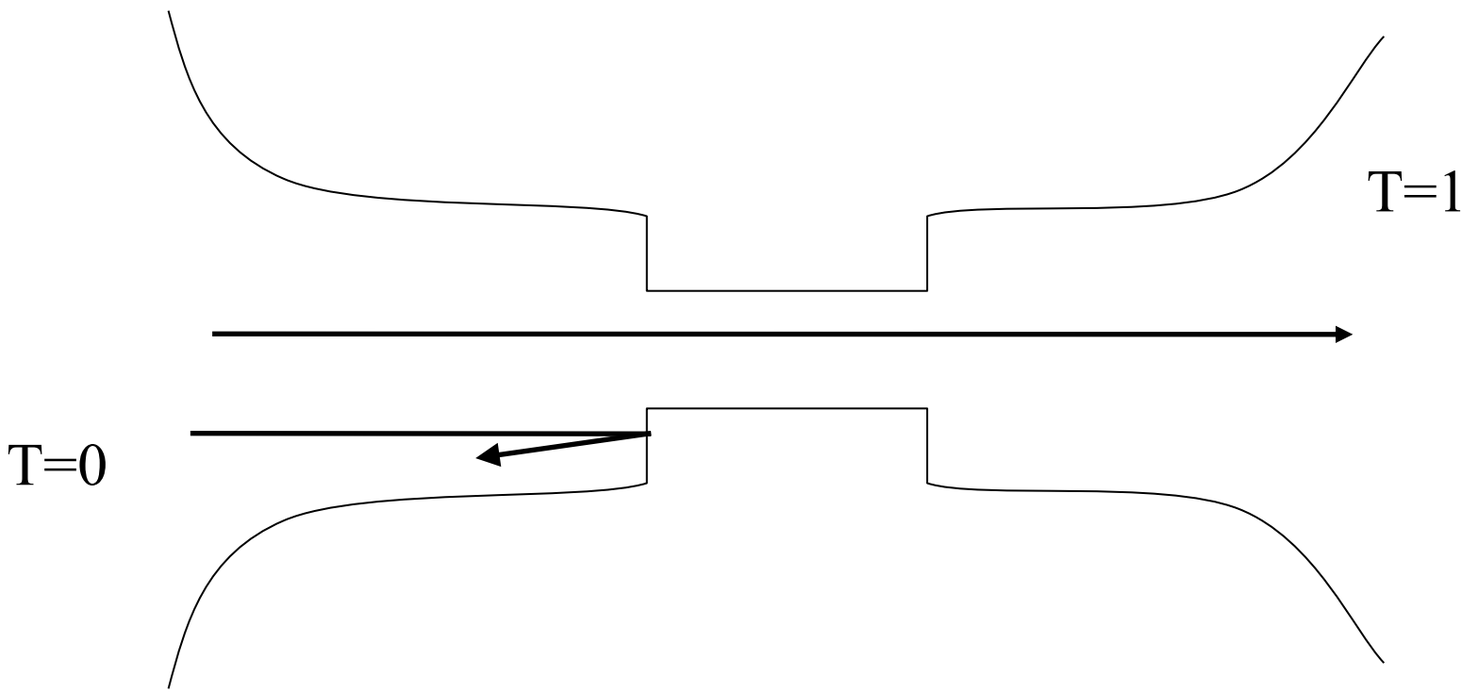
- Superexchange
- Basic Hopping
- Metallic Transport (e.g., Drude Model)
- Coulomb Blockade
- Kondo Effect
- Negative Differential Resistance
- Electron-Vibrational Effects

Landauer Coherent Conduction

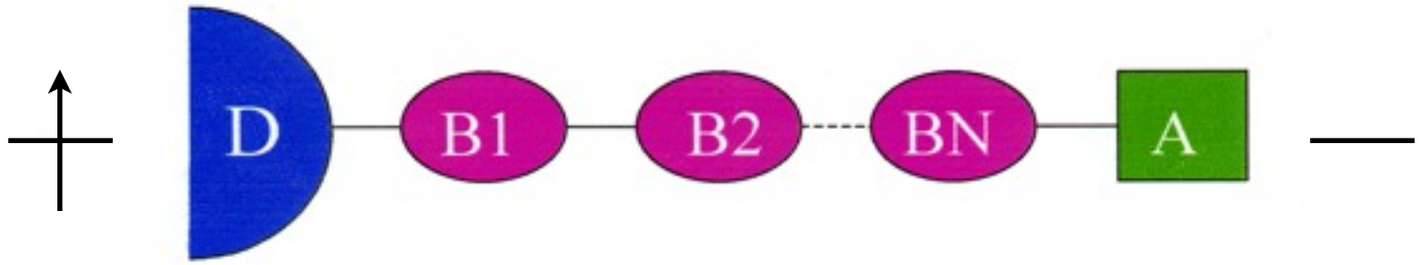
At the nanoscale, conductance is scattering...

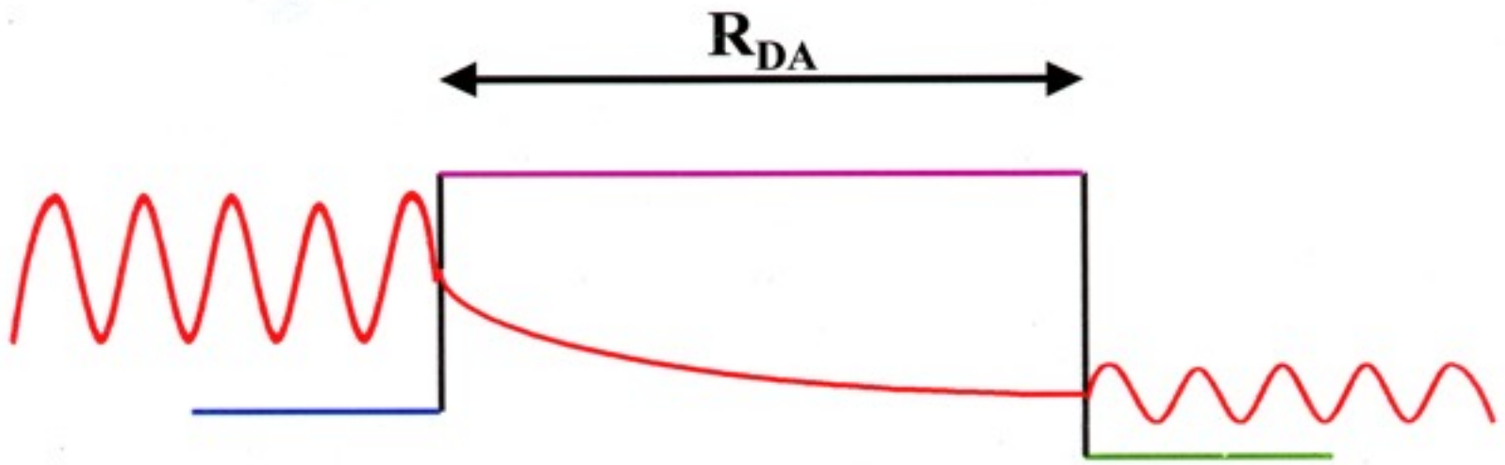
$$g = \frac{e^2}{h} \sum_i T_{ii}$$

T_{ii}= transition probability in the i^{th} transverse channel



Superexchange





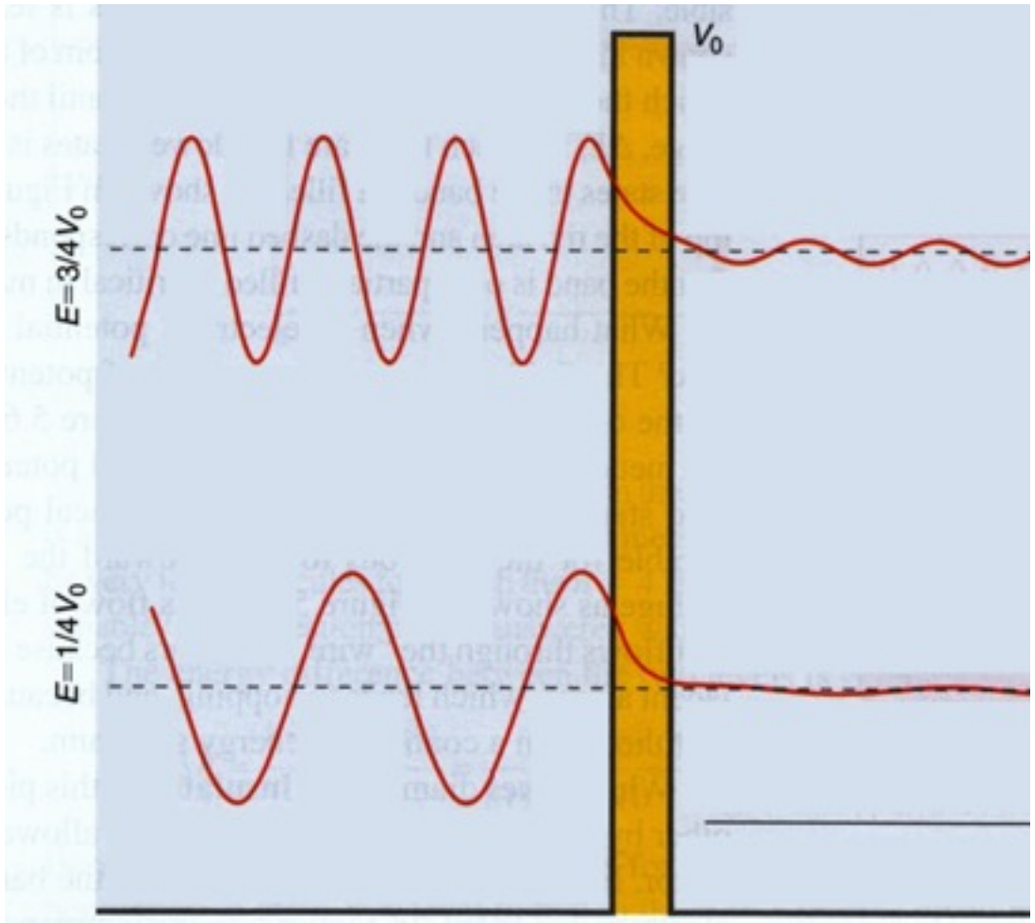
$$k_{ET} = A(T)\exp[-\beta R_{DA}]$$

Looks Like Tunneling

(Almost) Everything is Particle-In-A-Box...

- Finite probability of moving through barrier
- Greater probability for E close to V_0.
- Wavefunction falls off $e^{-\beta x}$

$$\beta = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

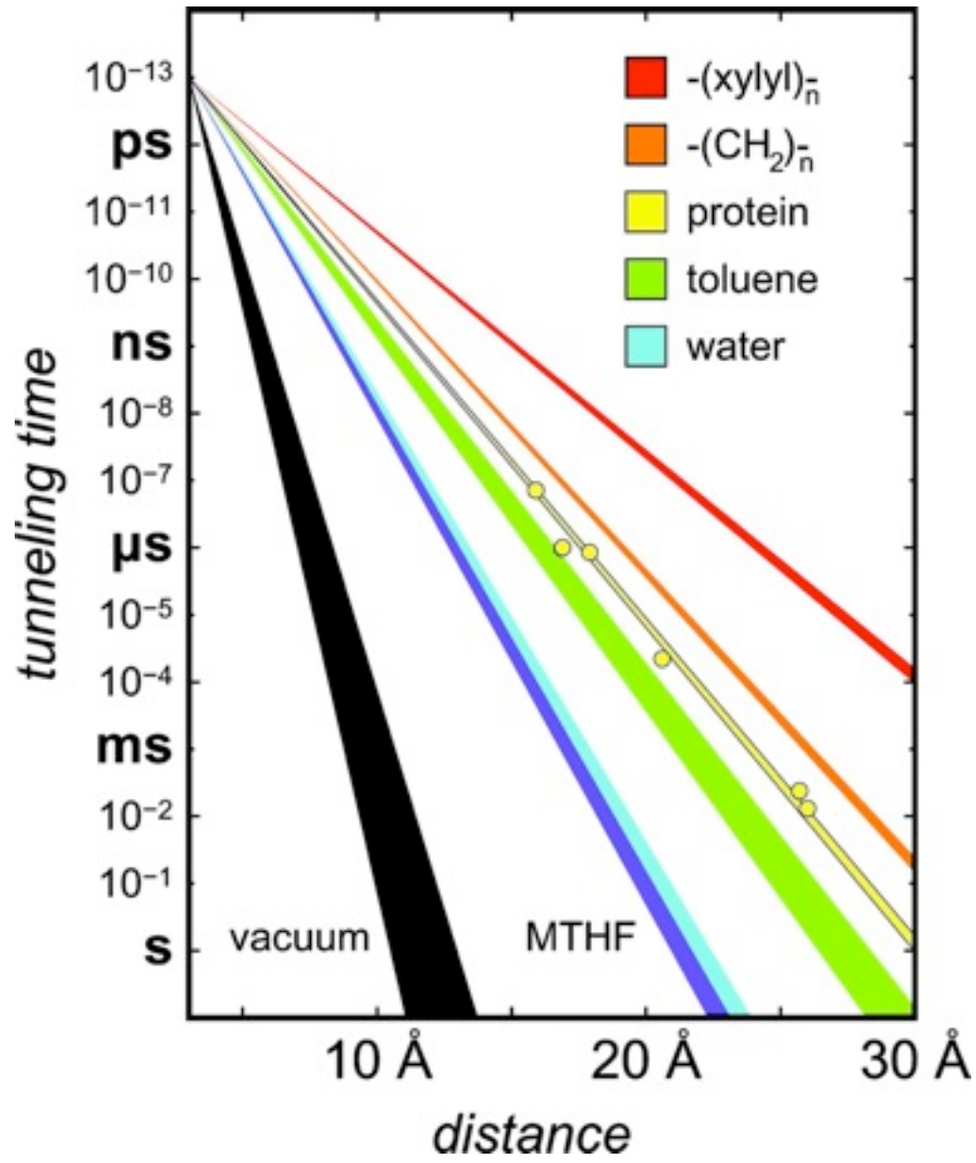


What are "normal" ß values?

Exponential Dependence

What are "normal" ß values?

- In Vacuum
  ~3–5 $Å^{-1}$
- Insulating
  (alkanes, protein, etc.)
  ~0.8–1.2 $Å^{-1}$
- Conjugated
  (alkenes, alkynes...)
  ~0.2–0.5 $Å^{-1}$



Gray, Winkler, *PNAS* **2005** vol. 102 p. **3534-3539**

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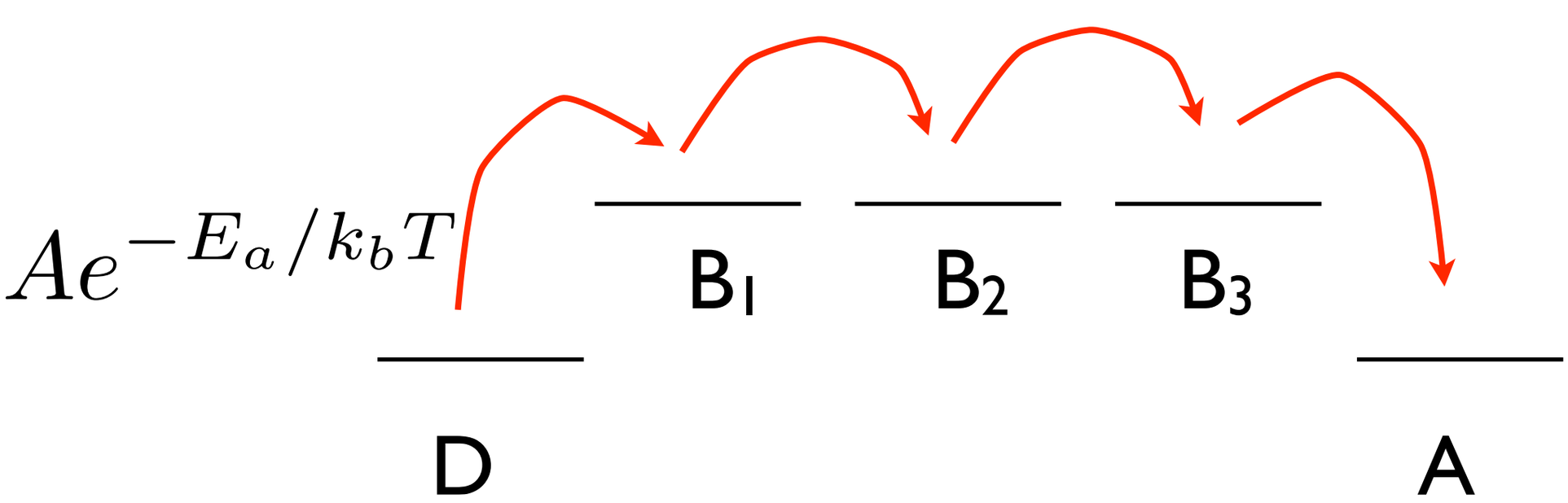
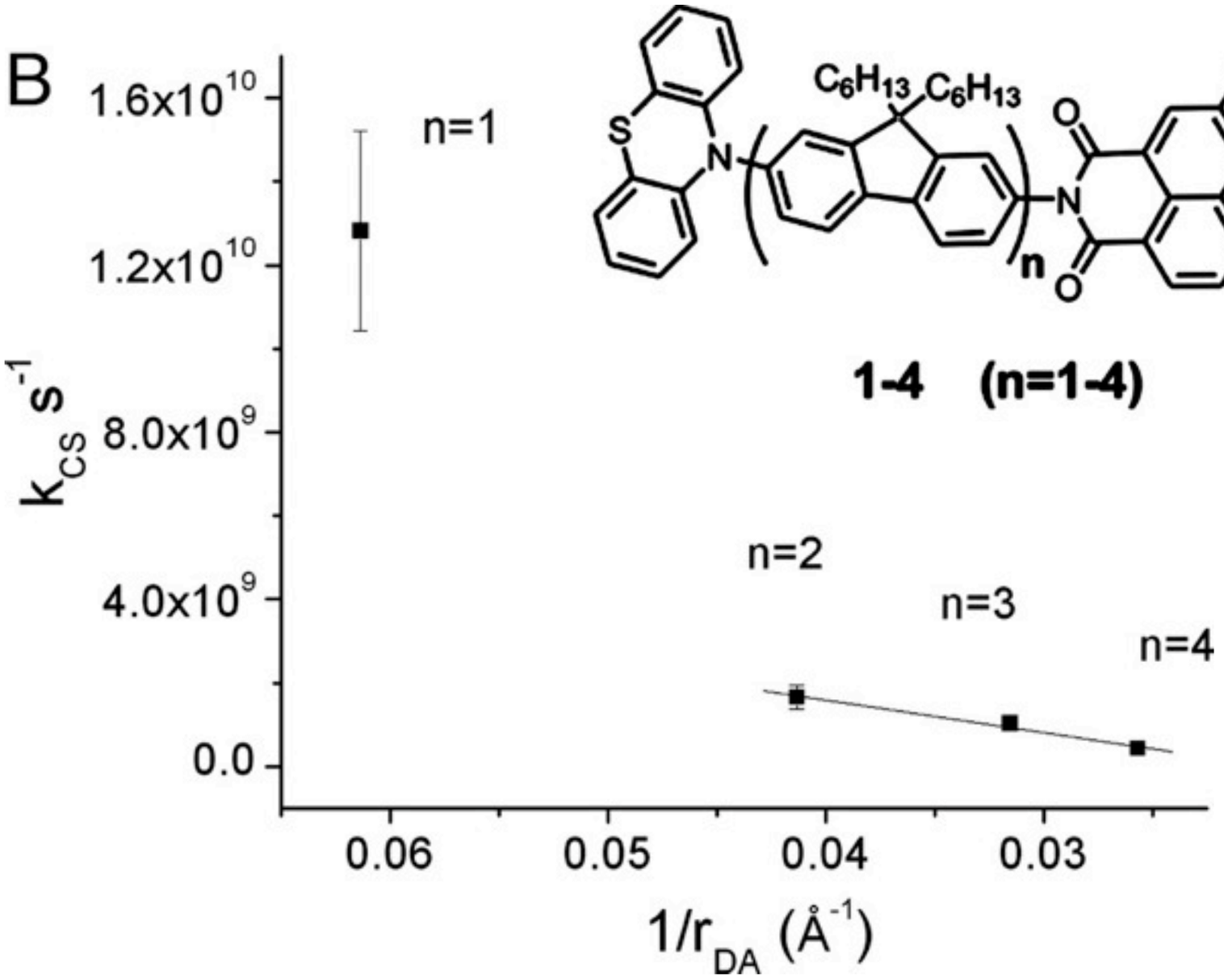
Hopping: Activated Transport

“Pay the Boltzmann Price”

1/R dependence



Superexchange to Hopping

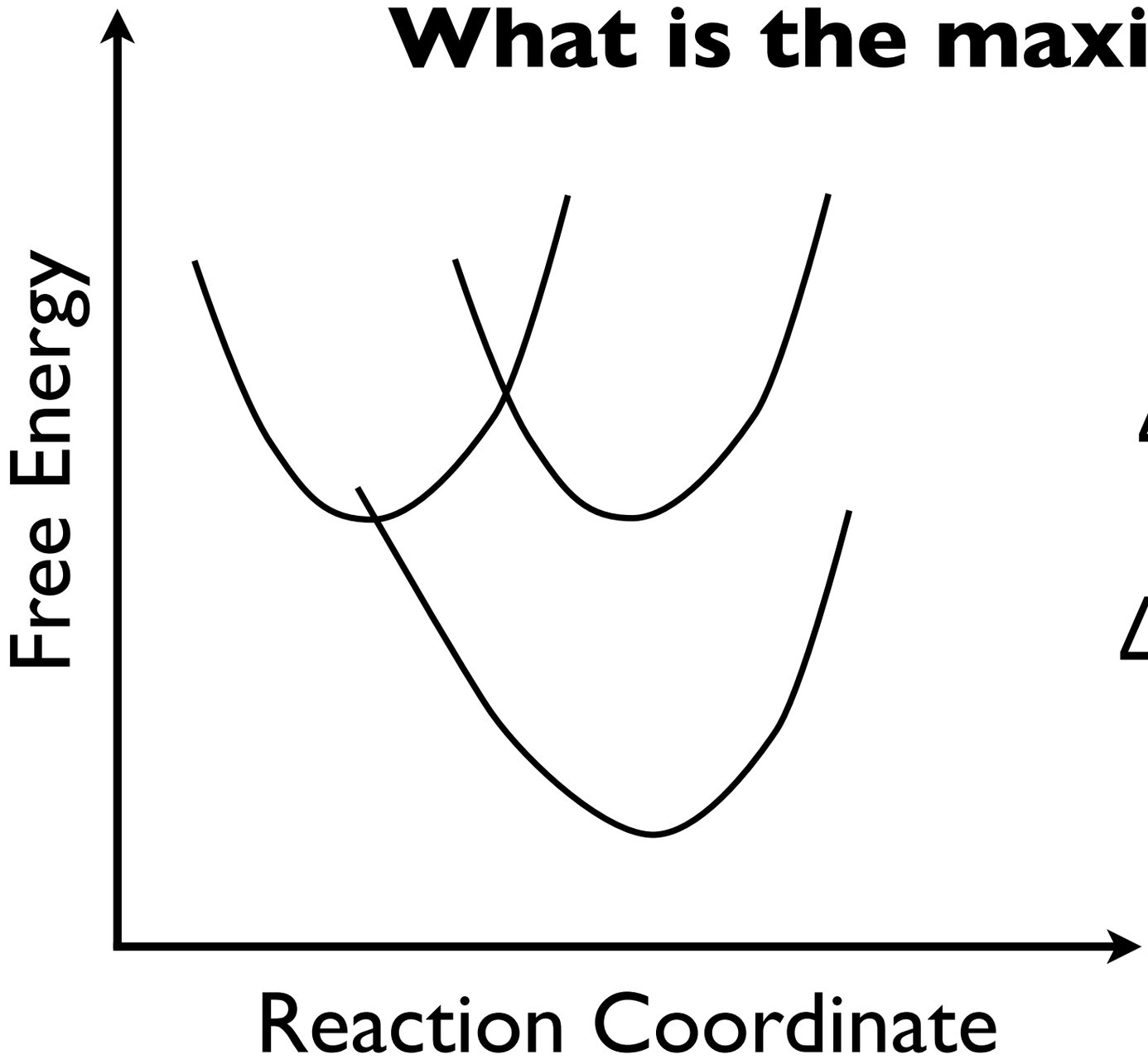


PNAS **2005** (*102*) p. 3540-3545

Marcus Theory

$$k_{CT} = Ae^{-(\Delta G^0 + \lambda)^2 / 4\lambda k_b T}$$

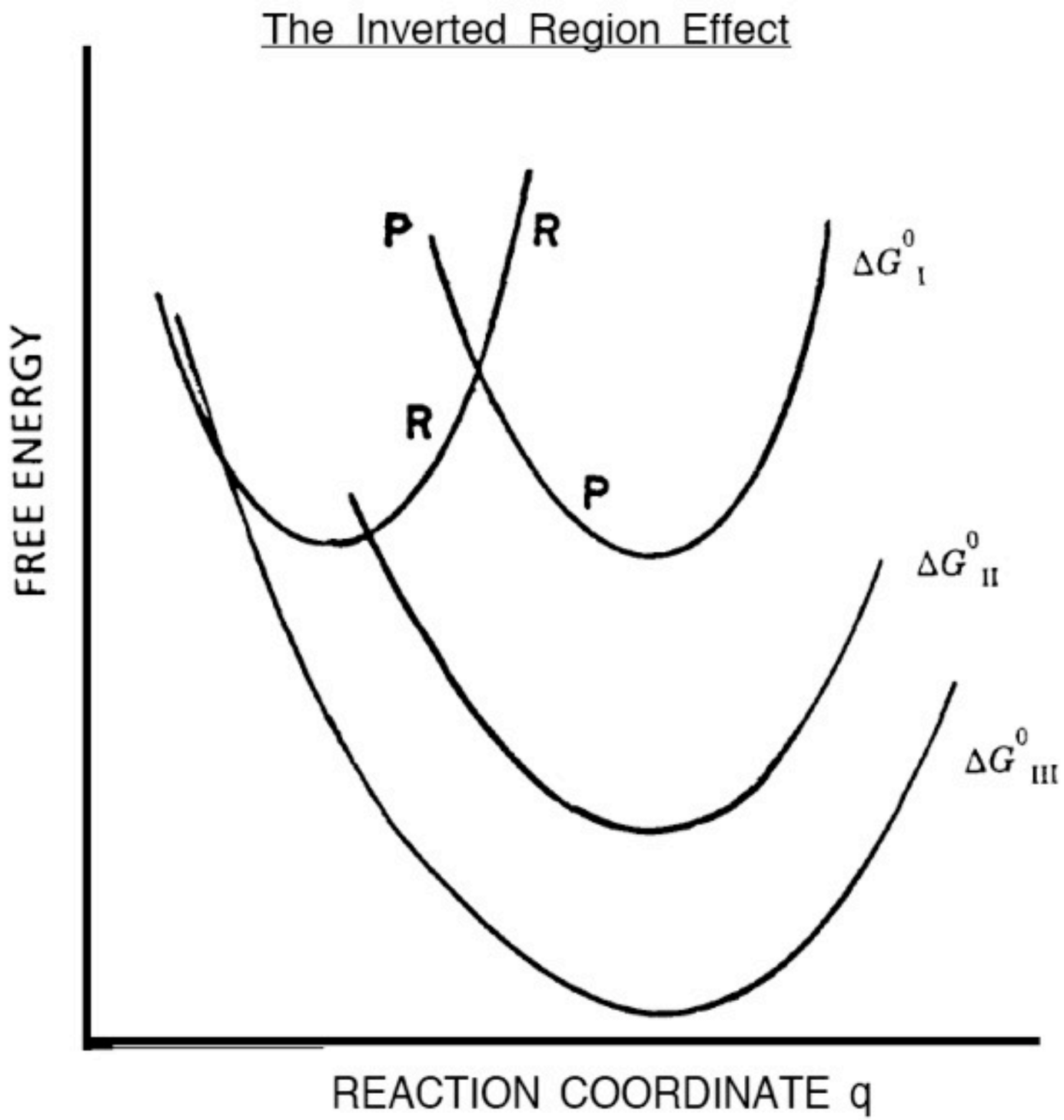
What is the maximum rate?

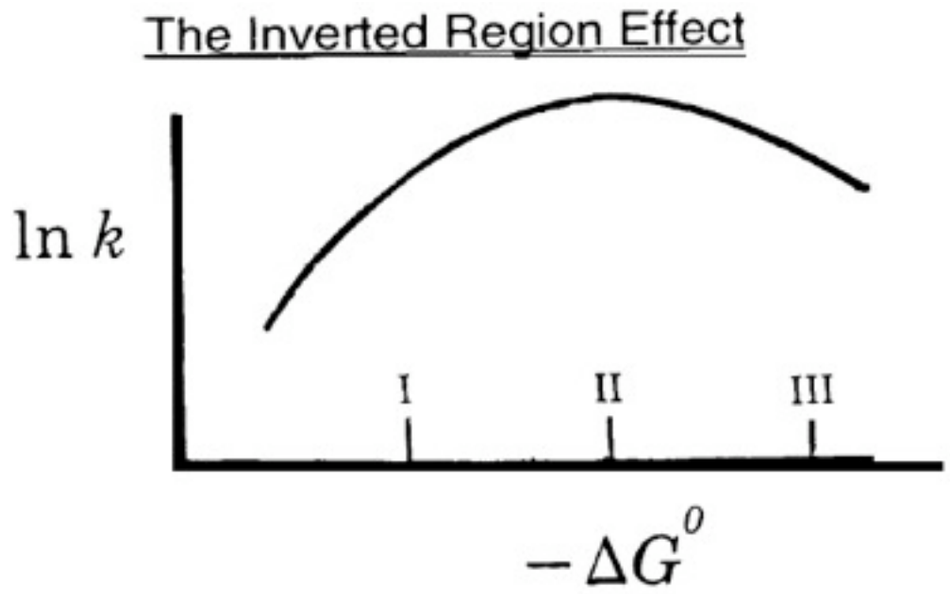


$\Delta G^0 = 0$

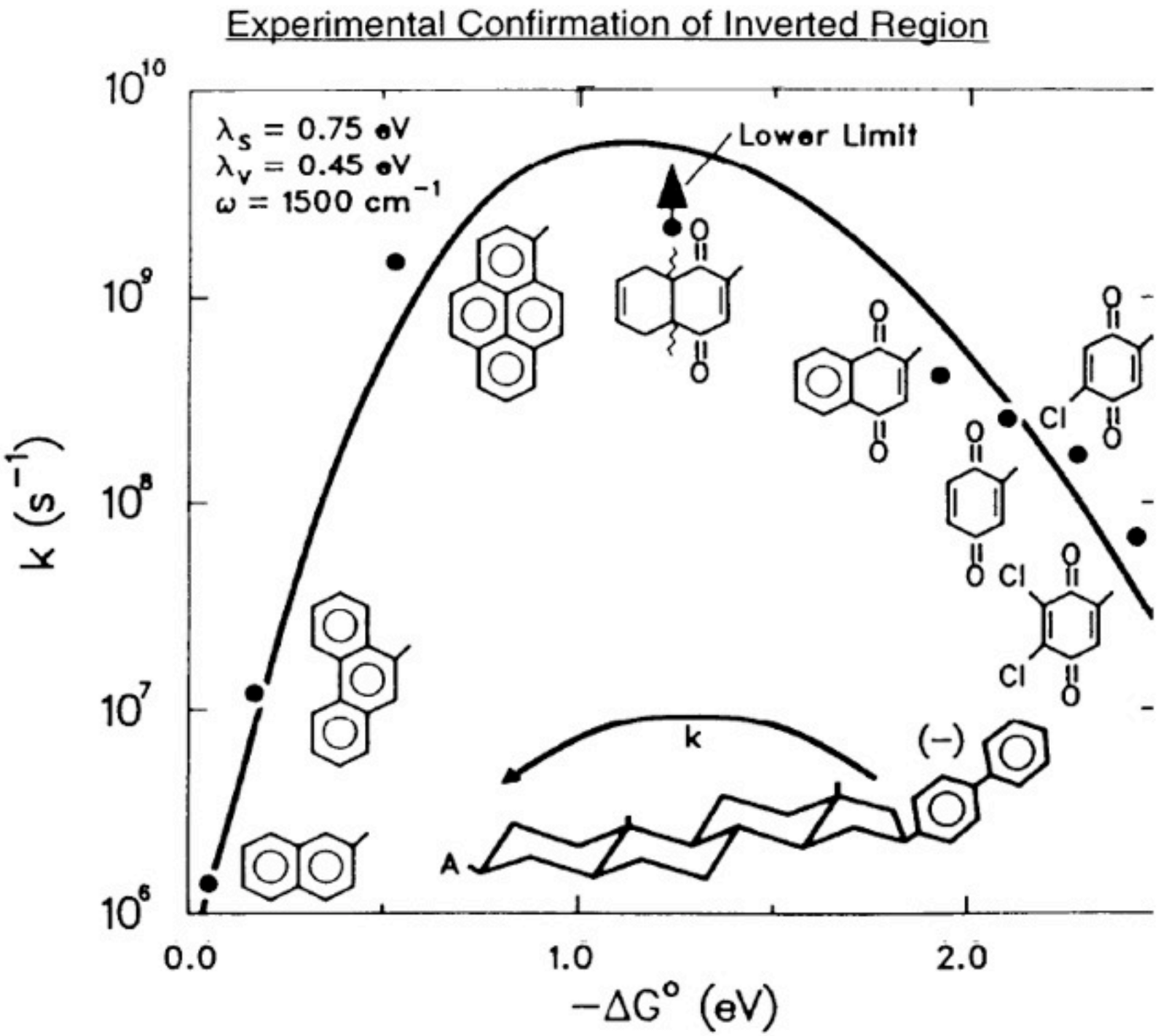
$\Delta G^0 = -\lambda$

Marcus Inverted Region





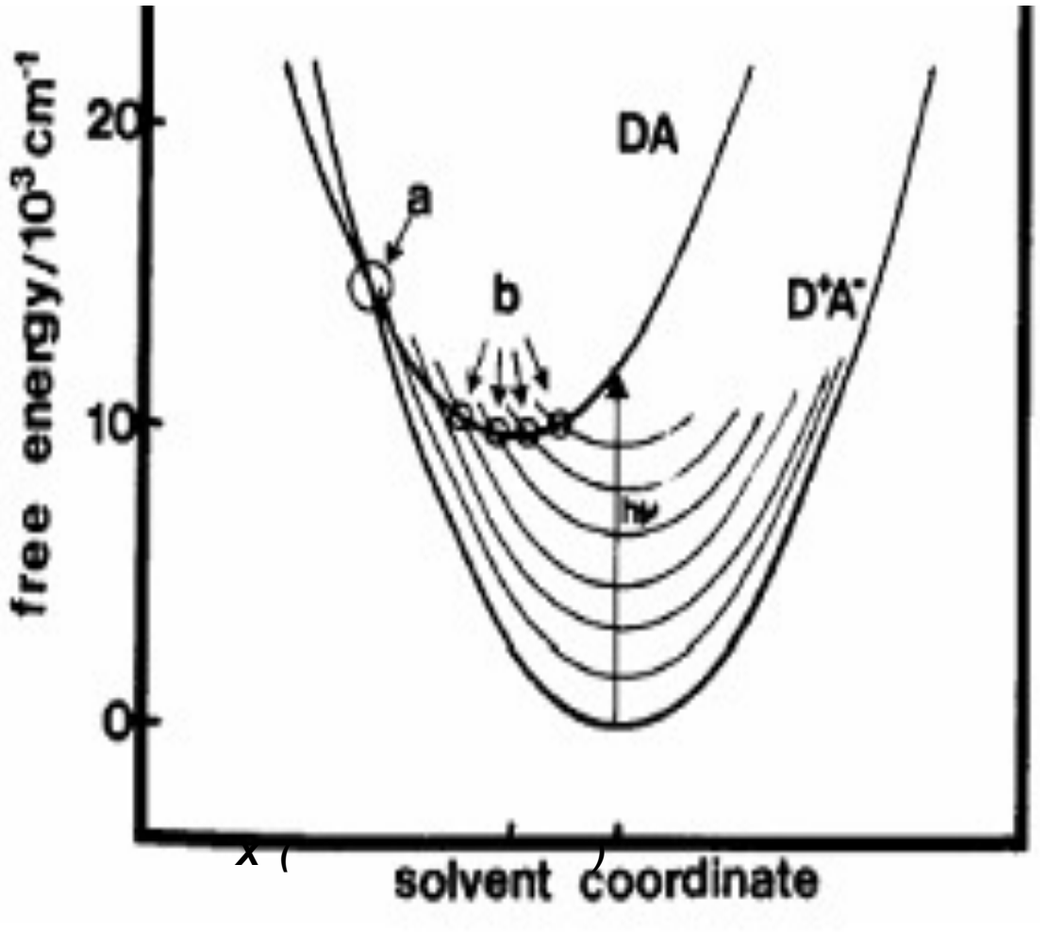
Experimental Proof: Inverted Region Exists



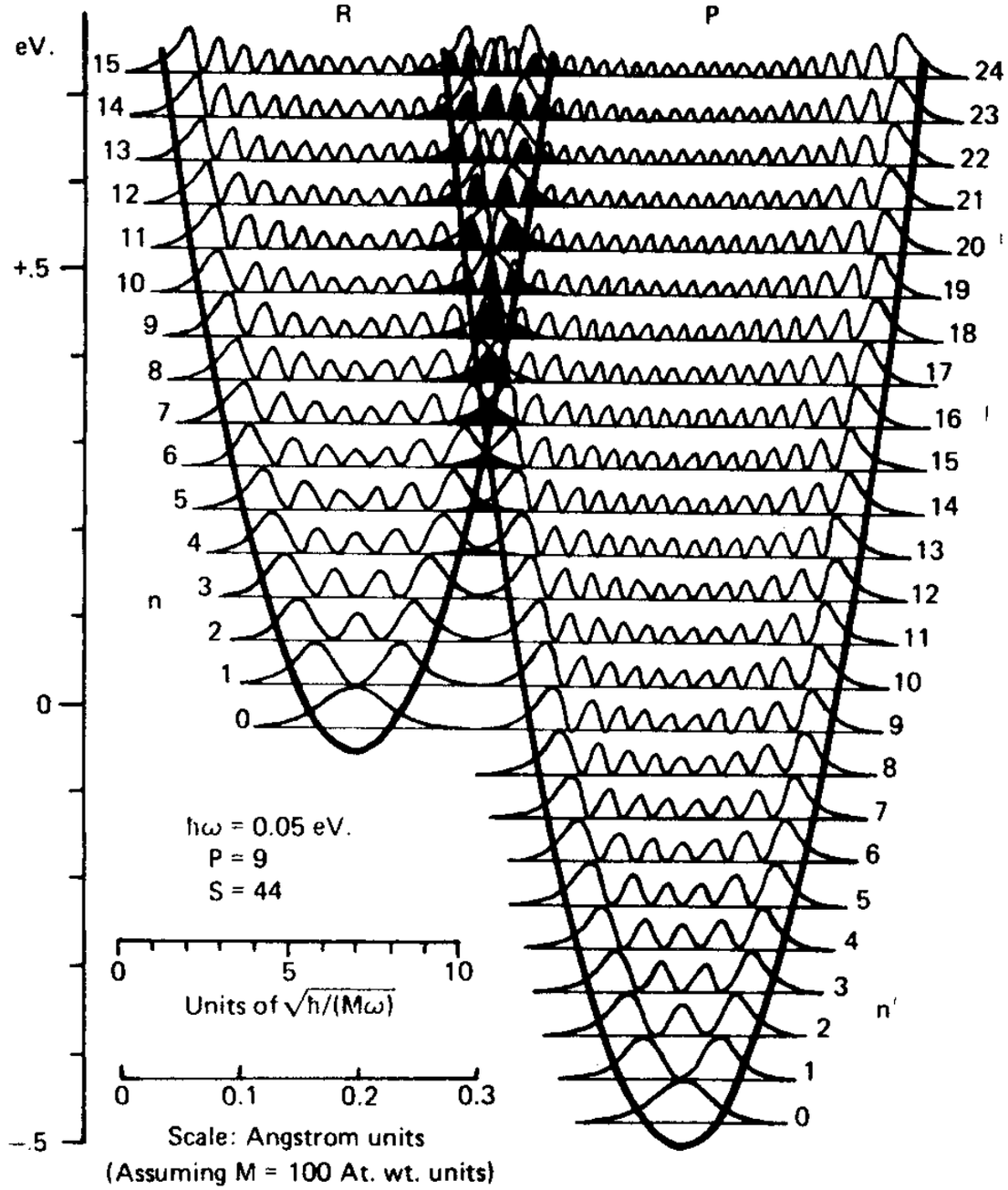
Miller, et. al. *JACS* **1984** *106* p.3047.

QM Treatment of Marcus Theory

From Rossky lecture:



J. Phys. Chem. **1996**, *100* p13148.



Reorganization Energies

$$\lambda = \lambda_{outer} + \lambda_{inner}$$

Environment
Solvent

e.g., Rossky lecture

Molecule
e.g., Σ(vibrational modes)

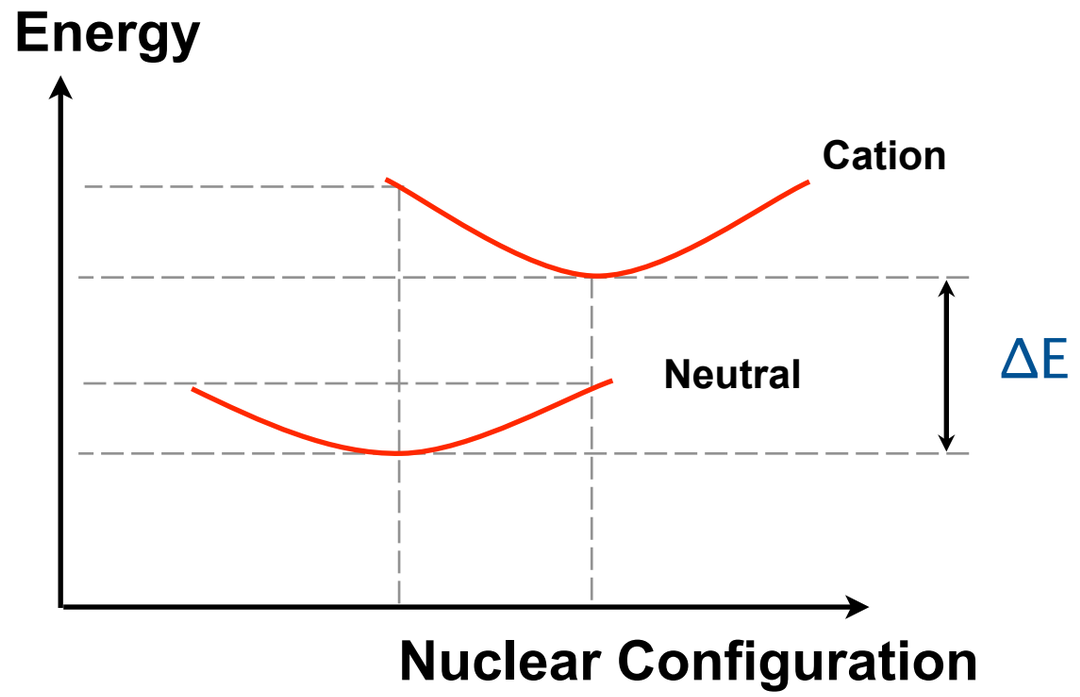
Dielectric Continuum

$$\lambda_s \approx (\Delta e)^2 [\frac{1}{2r_d} + \frac{1}{2r_a} - \frac{1}{R}][\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}]$$

Marcus-Hush Charge-Transfer Theory

Consider h^+ or e^- transfer:

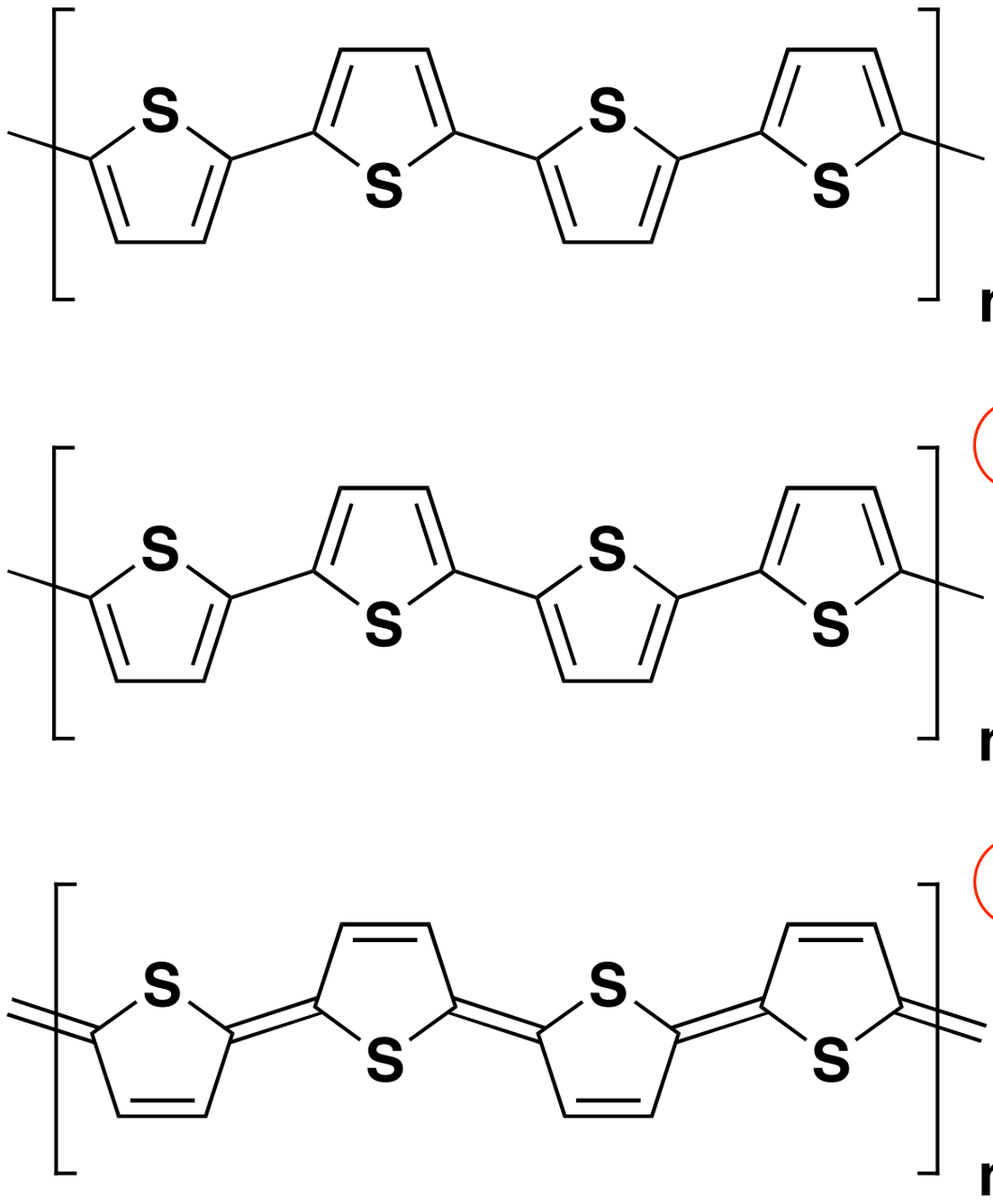
- Change in electronic structure (neutral ⇒ charge)
- Change in geometry reorganization of bonds, & environment



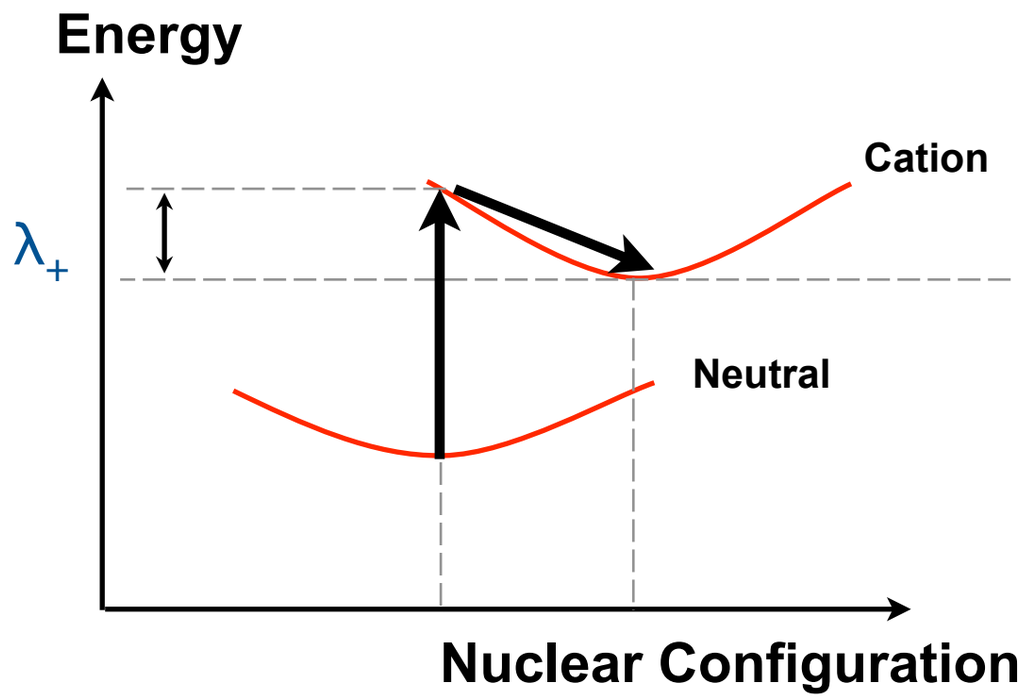
$$A^- + B \rightarrow A + B^-$$
$$A^+ + B \rightarrow A + B^+$$

$$k_{CT} = Ae^{-(\Delta G^0 + \lambda)^2/4\lambda k_b T}$$

Reorganization Energies: Geometric Relaxation

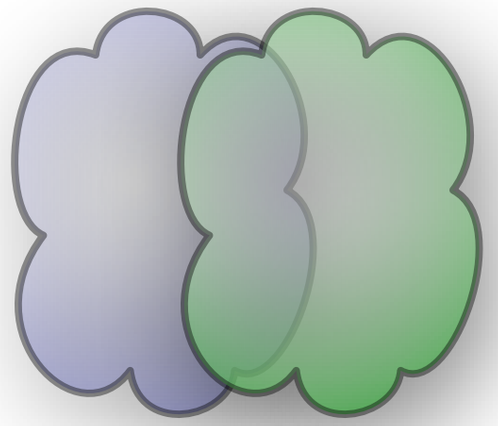


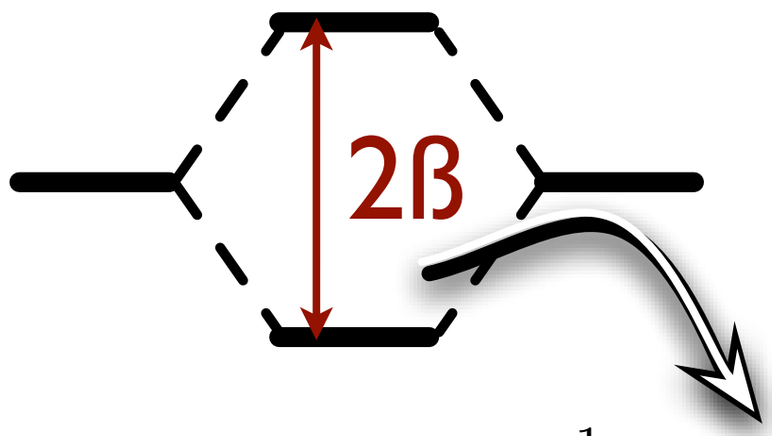
$$M^+ + M \rightarrow M + M^+$$



Intermolecular Interaction: Orbital Splitting Energies

For self-exchange:

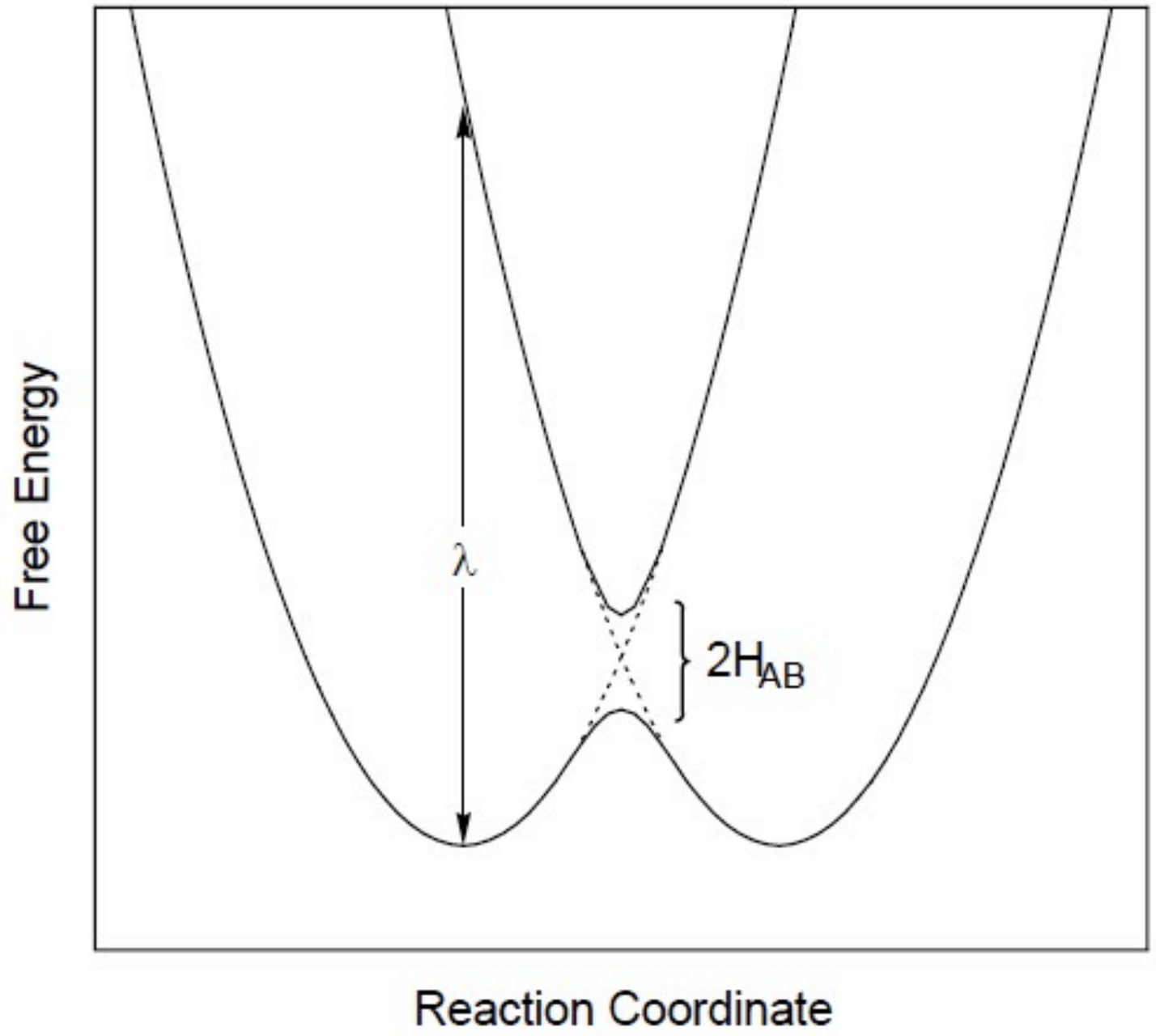




$$k = \left(\frac{\pi}{\lambda k_b T}\right)^{\frac{1}{2}} \frac{H_{ab}^2}{\hbar} e^{-\lambda/4k_b T}$$

Note: electronic coupling has exponential fall-off

Alternate View of H_{ab}



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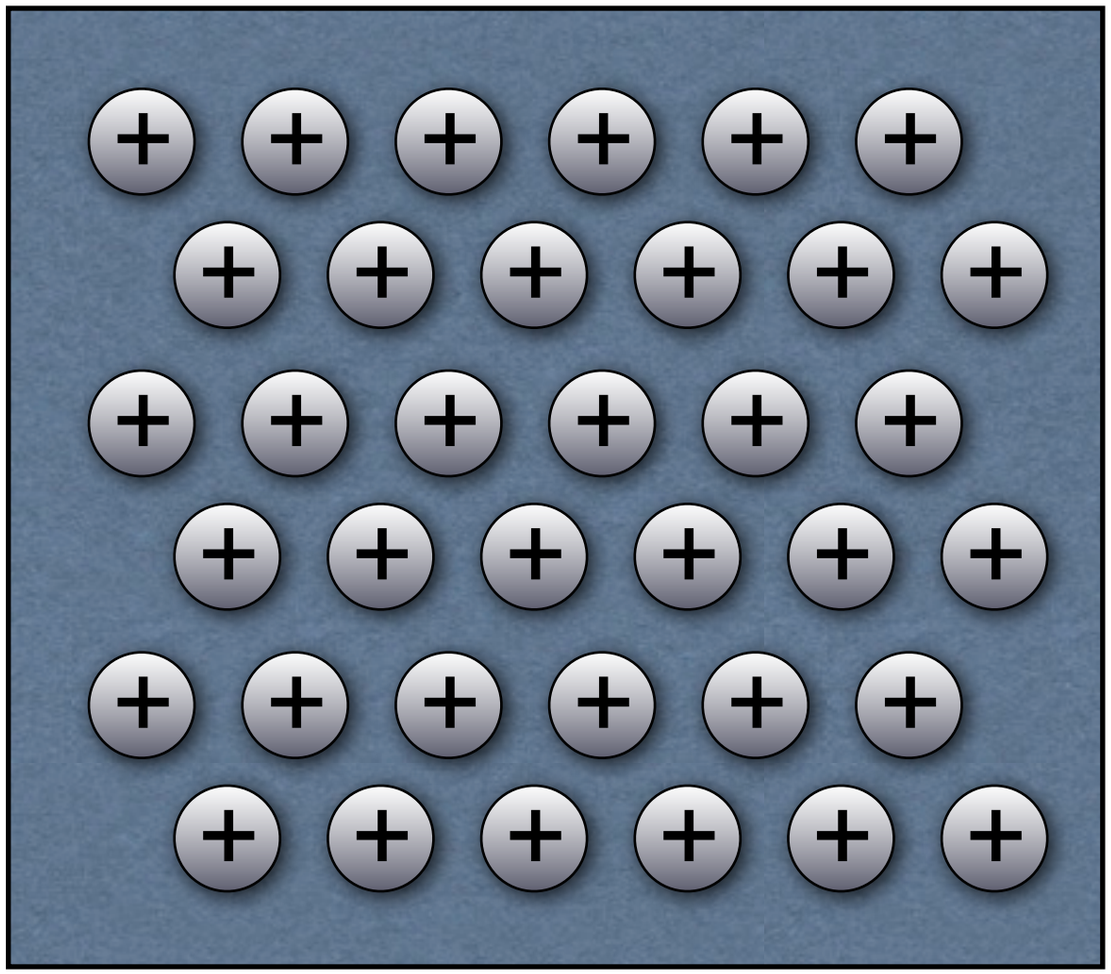
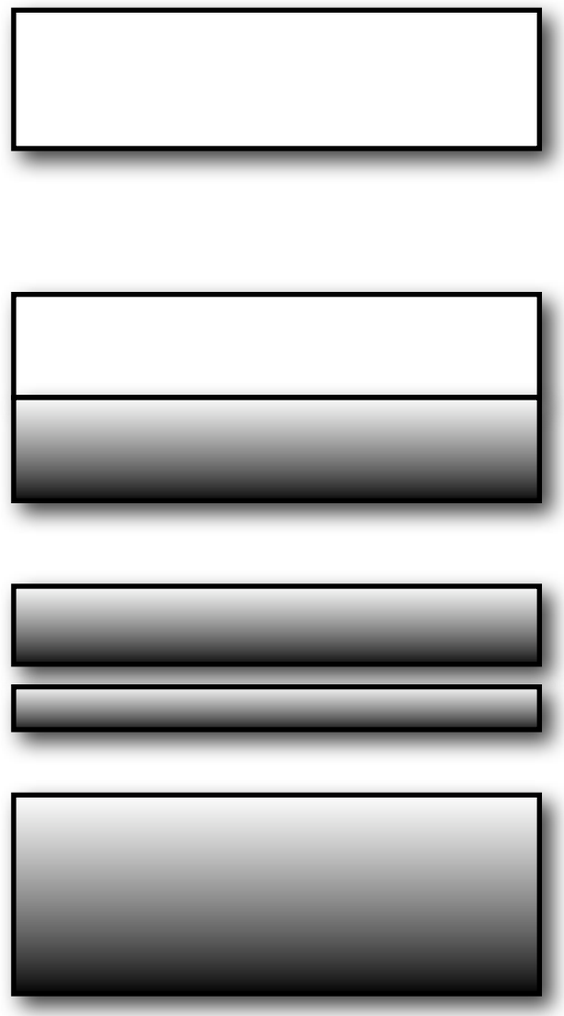
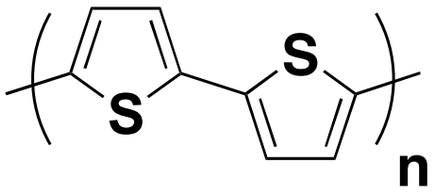
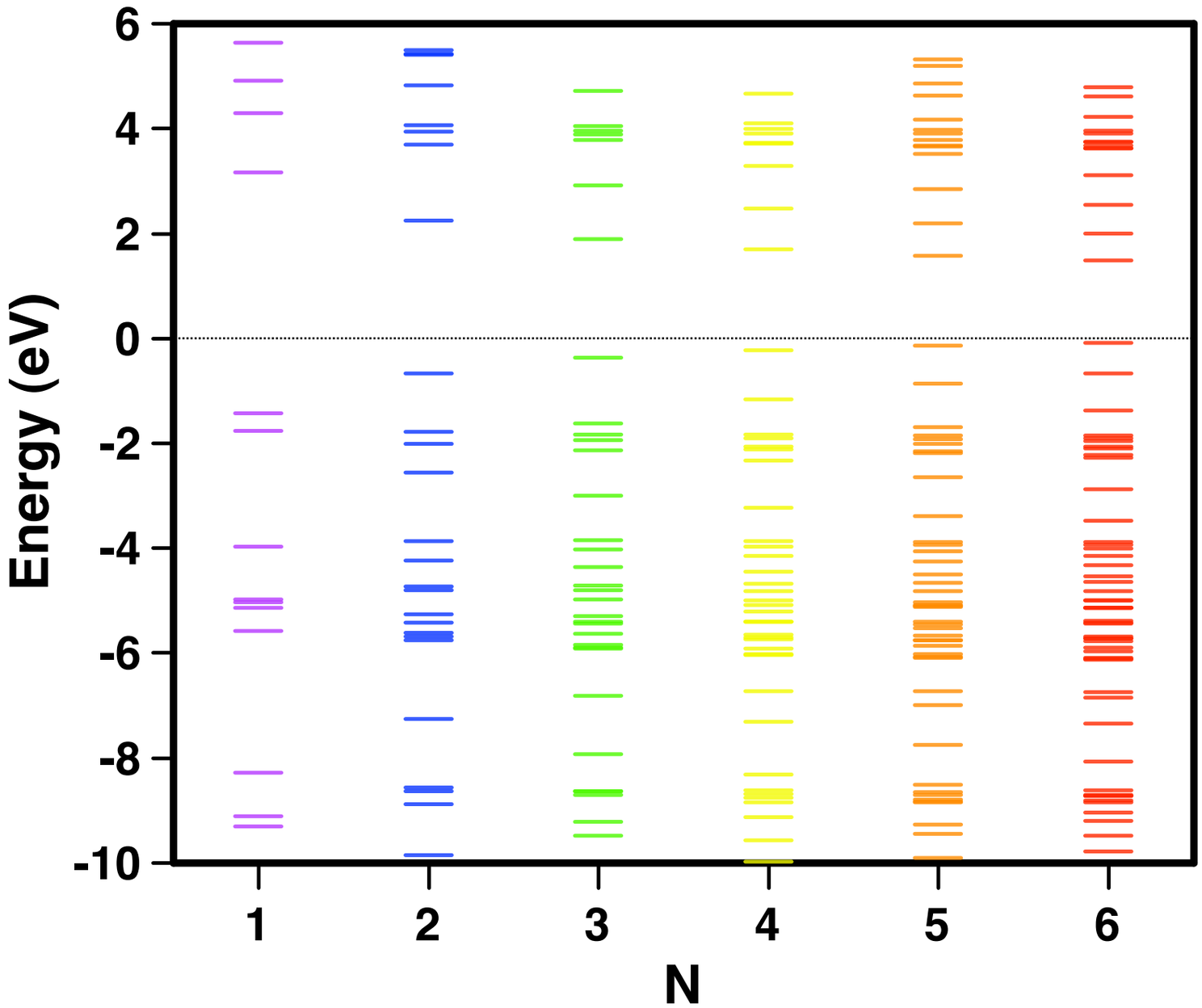
Metallic Transport: "Electron Sea" Model of Metals

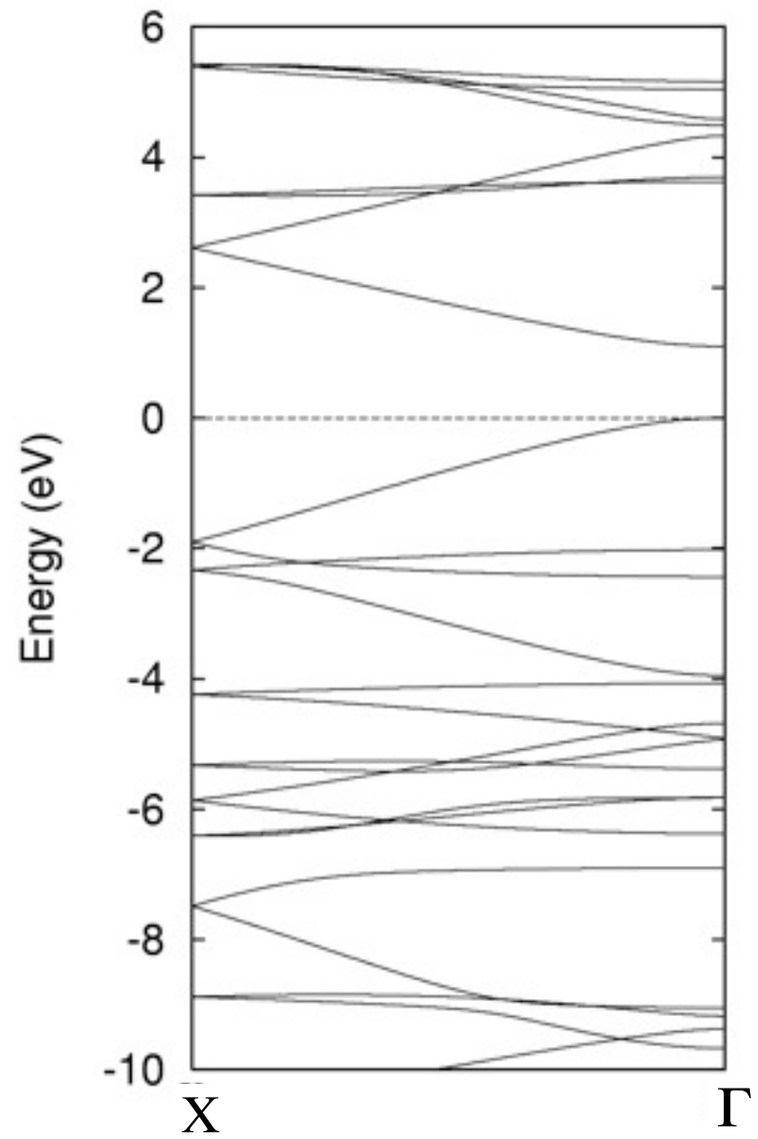




Evolution of Band Structure







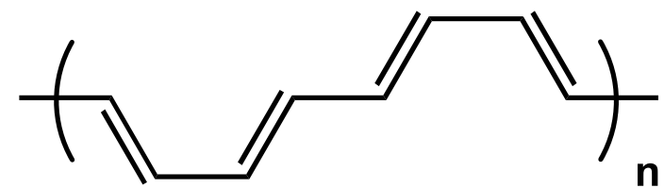
Hutchison, et. al. *Phys. Rev. B* **2003** *68* no.035204.

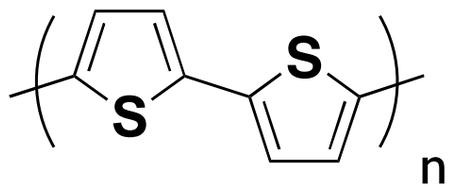
Interpretation of Band Diagrams

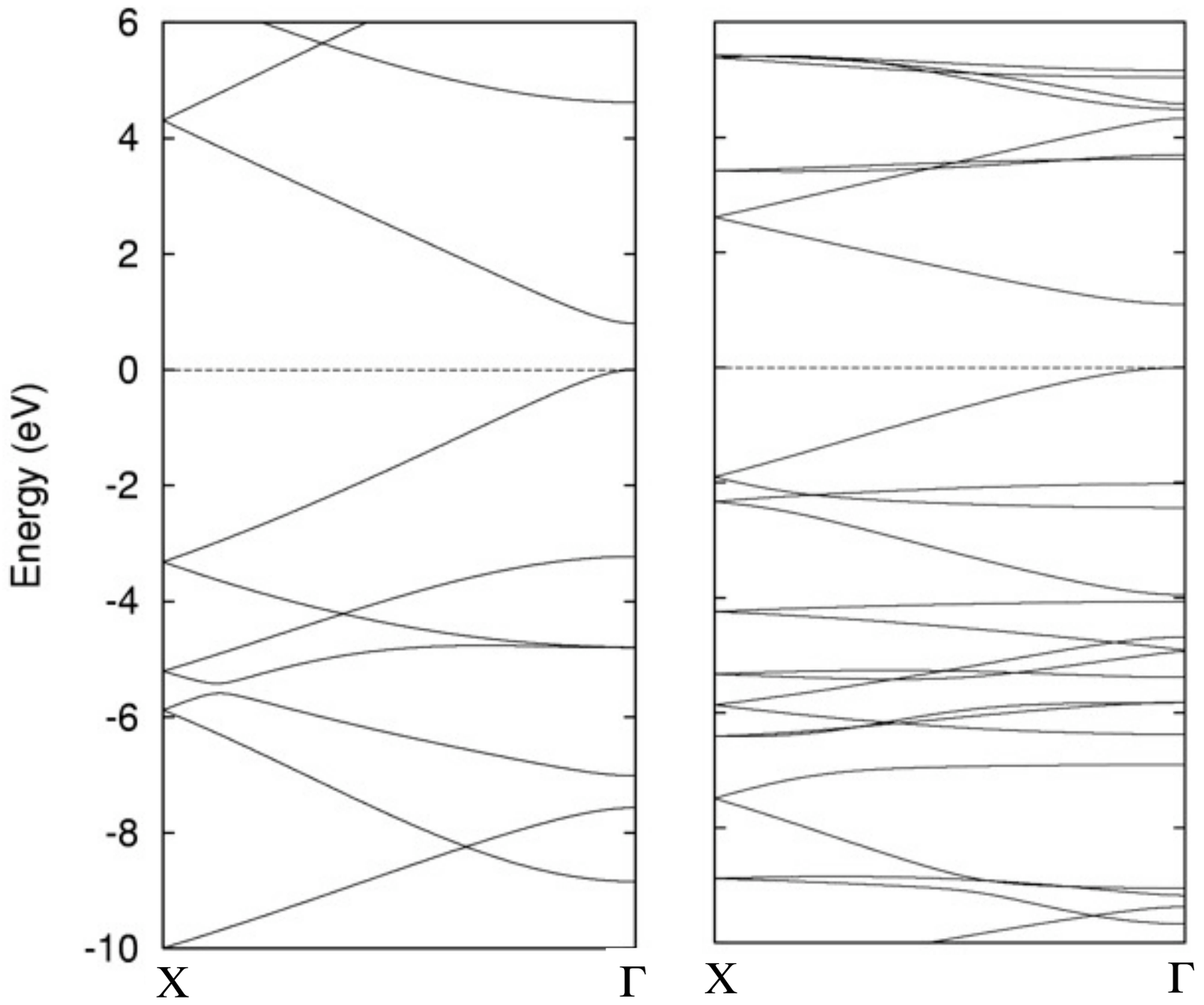
Diagram shows energy as a function of Brillouin zone

- Broad bands: delocalized
- Thin bands: highly localized (e.g. S atom)
- Direct band gap
- Curvature of bands: effective mass of h^+ or e^-

trans-cisoid-polyacetylene

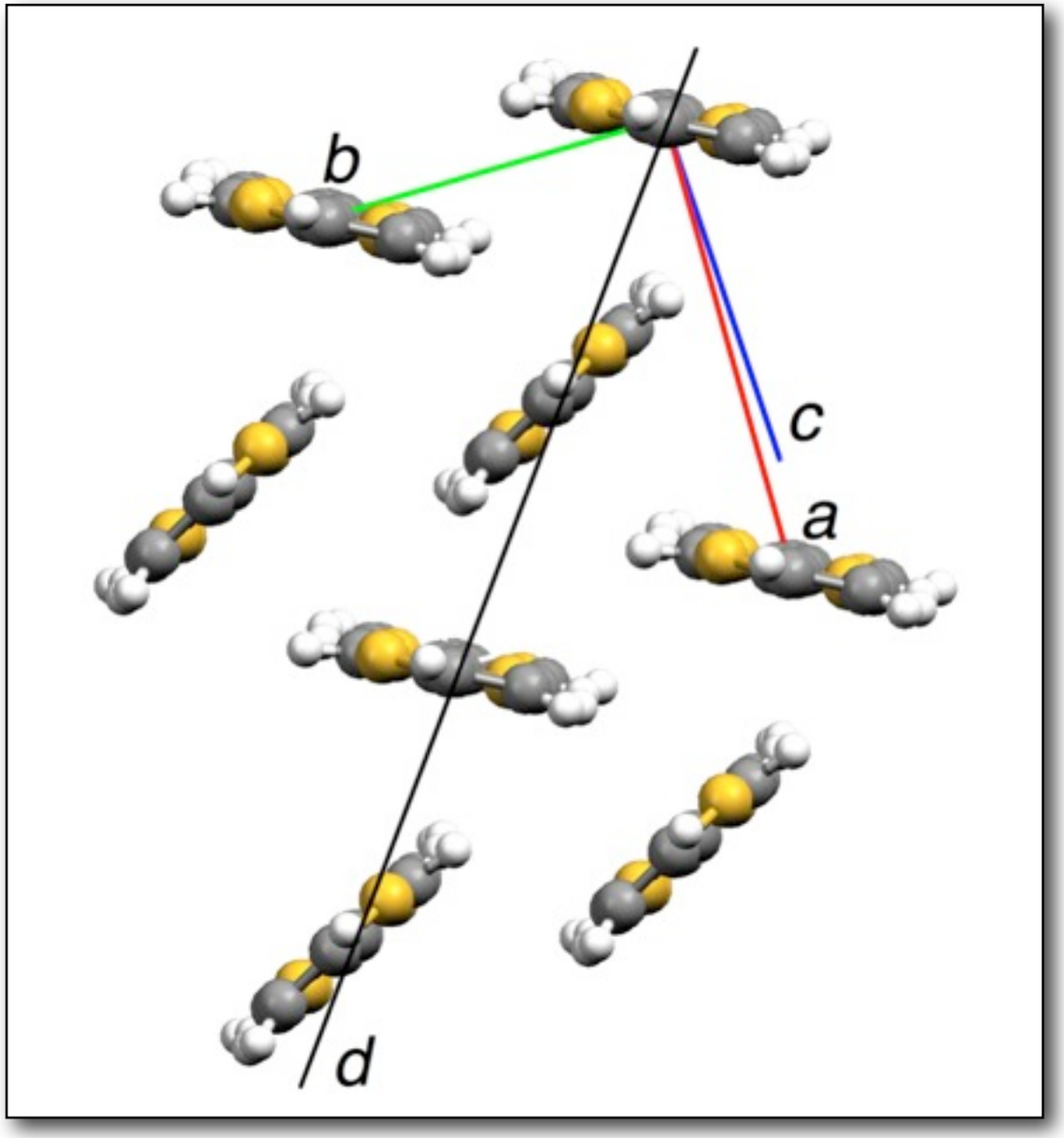






Hutchison, et. al. *Phys. Rev. B* **2003** *68* no.035204.

3D Band Structure: Possibly Anisotropic



Drude Model

- Limit on e^- conductance is scattering
- Treat as "electron gas" of non-interacting electrons
- Collision between e^- and positive ions, creates "drag" γ

$$\gamma = m/\tau$$

$$F = ma$$

$$m\frac{d}{dt}\langle\vec{v}\rangle = q\vec{E} - \gamma\langle\vec{v}\rangle$$

steady state:

$$\langle\vec{v}\rangle = \frac{q\tau}{m}\vec{E} = \mu\vec{E}$$

Effective Masses

$$F = ma$$

from quantum mechanics: $$a = \frac{1}{\hbar^2} \cdot \frac{d^2\varepsilon}{dk^2} qE$$

$$F = qE$$

simplifying...

$$\frac{1}{m^*} = \frac{\left[\frac{d^2\varepsilon}{dk^2}\right]}{\hbar^2}$$

from Drude model...

$$\langle \vec{v} \rangle = \frac{q\tau}{m}\vec{E} = \mu\vec{E}$$

Comparisons of Effective Masses

Material	Hole	Electron
Si	0.56	1.08
Ge	0.37	0.55
P(Thio)	0.14	0.15
P(Pyr)	0.21	0.24

(unit is fraction of electron mass)

Hutchison, et. al. *Phys. Rev. B* **2003** *68* no.035204.

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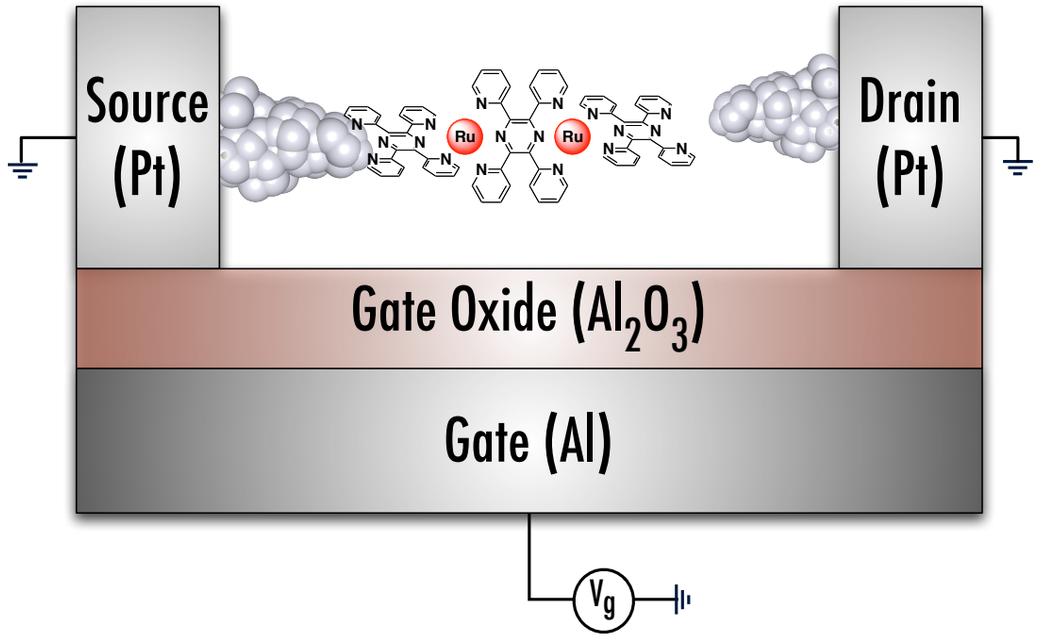
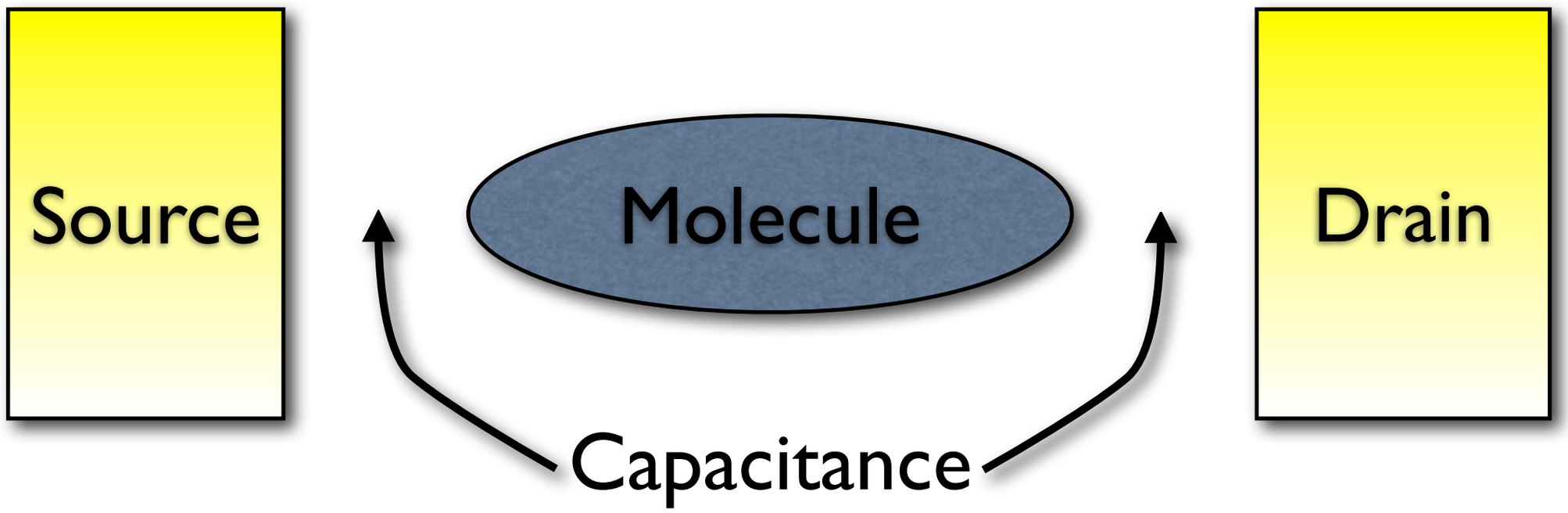
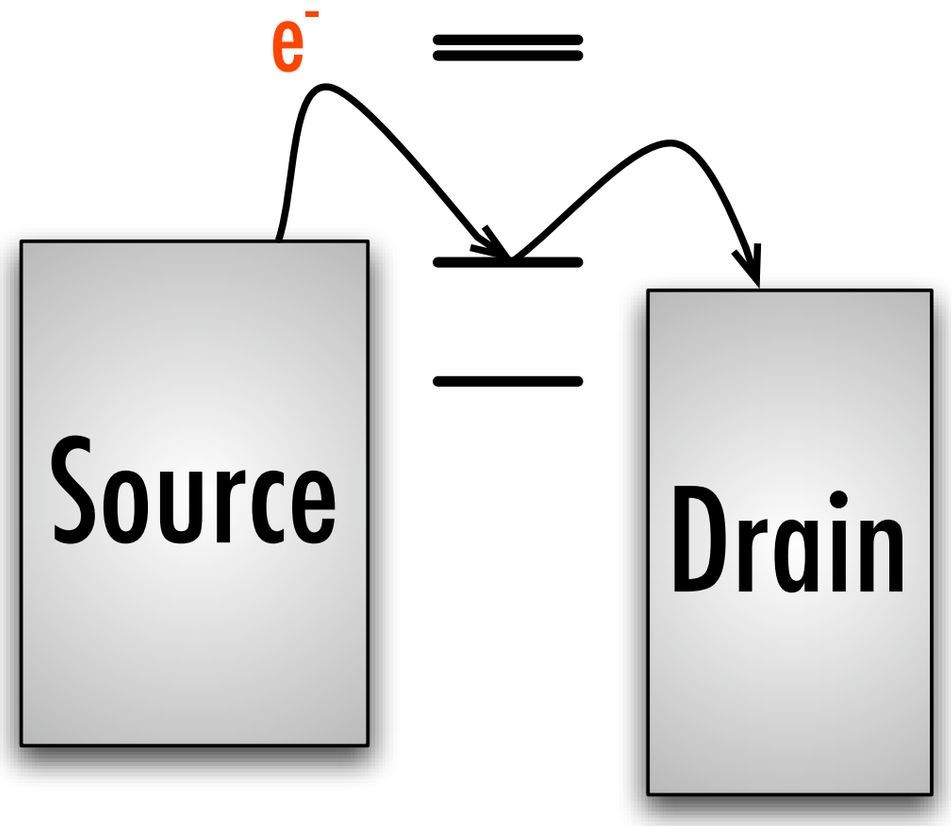
Coulomb Blockade

We saw this already...



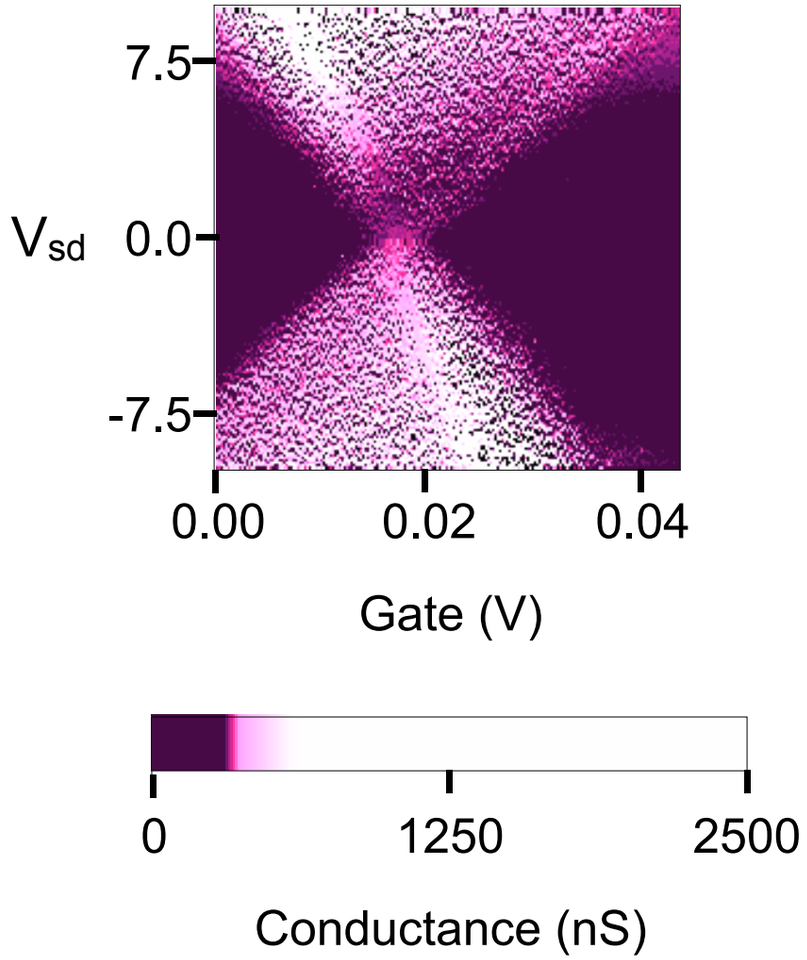


Coulomb Blockade in $[Ru_2(tppz)_3]^{+4}$

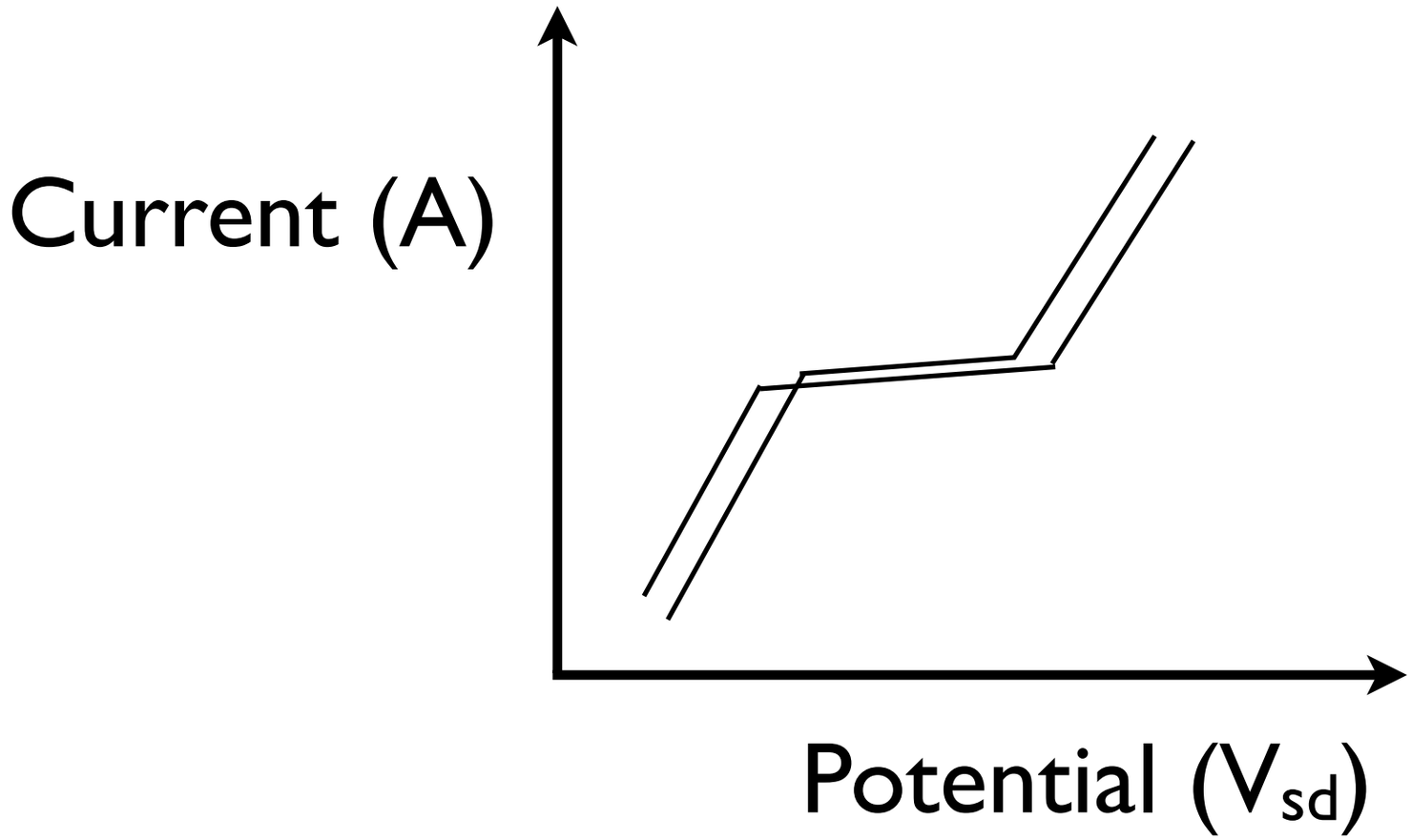


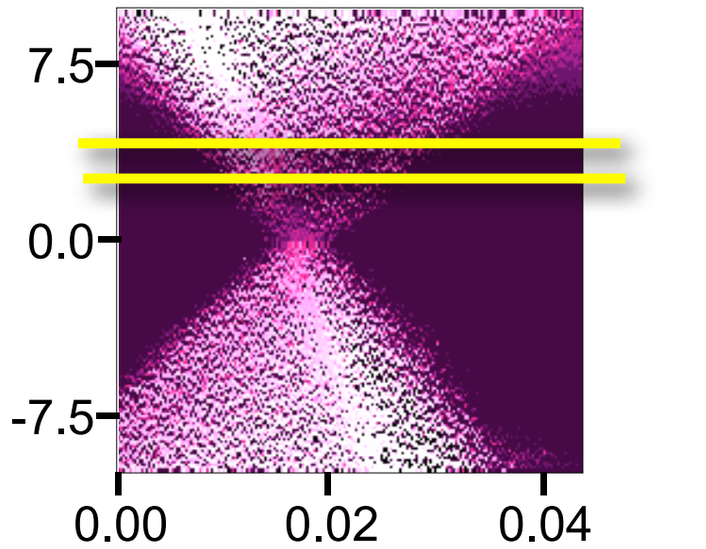
Charge passes when source, drain and molecule bridge electronic states are aligned

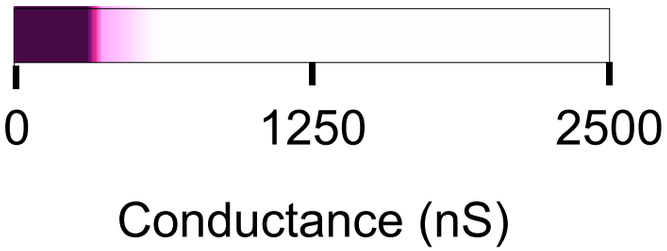
4K Temp. Single-Molecule Coulomb Blockade Transistor



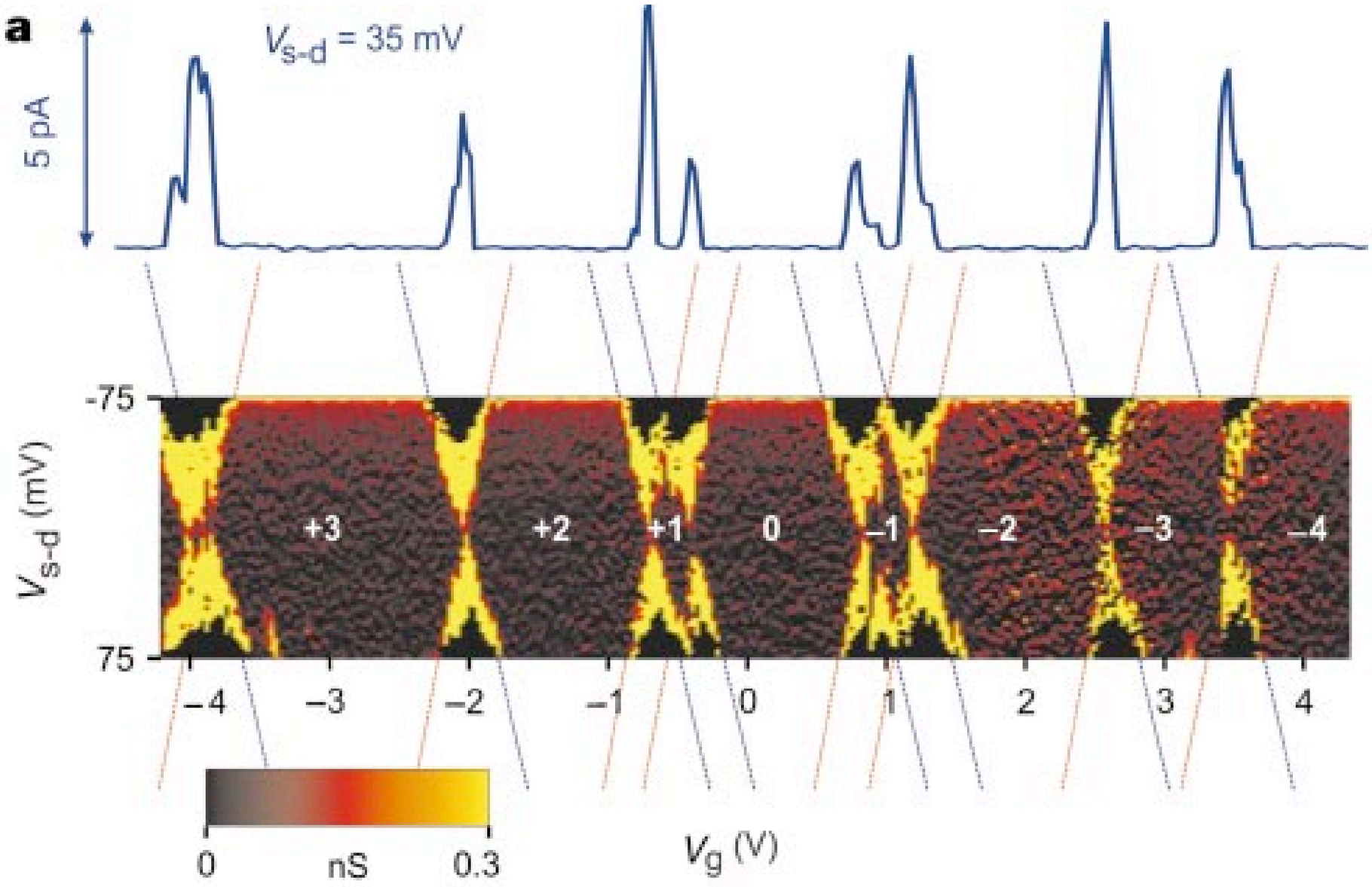
Coulomb Blockade I/V Curves







Be Careful... Multiple Coulomb Blockade?



Nature (**2003**) *425* p. 698-701

How do you know this is **one** molecule?